



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/EP99/00255 <b>(22) International Filing Date:</b> 12 January 1999 (12.01.99)  <b>(30) Priority Data:</b> 98830090.1 24 February 1998 (24.02.98) EP 60/086,889 27 May 1998 (27.05.98) US  <b>(71) Applicant (for all designated States except US):</b> PIRELLI PNEUMATICI S.P.A. [IT/IT]; Viale Sarca, 222, I-20126 Milano (IT).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> PAVAN, Federico [IT/IT]; Via Pilati, 4A, I-50136 Firenze (IT). RATTI, Giuseppina [IT/IT]; Via Valassina, 14, I-20038 Seregno (IT). CAVALLOTTI, Pietro, Luigi [IT/IT]; Viale Abruzzi, 72, I-20131 Milano (IT). BOZZINI, Benedetto [IT/IT]; Viale Pasubio, 1, I-20154 Milano (IT).  <b>(74) Common Representative:</b> PIRELLI PNEUMATICI S.P.A.; Viale Sarca, 222, I-20126 Milano (IT).		<b>(81) Designated States:</b> AL, AU, BR, BY, CA, CN, CZ, ID, JP, KR, LT, LV, MK, MX, RO, RU, SI, SK, TR, UA, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> A SURFACE-TREATED STEEL WIRE FOR REINFORCING STRUCTURES FOR ARTICLES OF MANUFACTURE MADE OF ELASTOMERIC MATERIAL AND AN ARTICLE OF MANUFACTURE COMPRISING THE SAME  <b>(57) Abstract</b>  A surface-treated steel wire for reinforcing structures for articles of manufacture made of vulcanized elastomeric material, in which the said wire is coated with a layer of metal alloy, wherein the said alloy is a zinc/manganese binary alloy comprising from 0.3 to 4.9 % by weight of manganese.		

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"A surface-treated steel wire for reinforcing structures for articles of manufacture made of elastomeric material and an article of manufacture comprising the same"

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5       The present invention relates to a steel wire, for reinforcing structures for articles of manufacture made of vulcanized elastomeric material, which is surface-coated with a metal alloy and an article of manufacture comprising said wire buried in a vulcanized elastomeric material. The present invention further relates to a process for coating  
10   said wire with said alloy.

More specifically, the present invention relates to a steel wire coated with a zinc/manganese alloy in which the manganese content is less than 4.9% by weight

15       The present invention also relates to a reinforcing structure comprising the said wire and to an article of manufacture made of a vulcanized elastomeric material comprising said reinforcing structure.

As is known, tyres, as well as many other articles of manufacture made of vulcanized elastomeric material, usually incorporate reinforcing structures made with metal cords, each of which is composed of a plu-  
20   rality of metal wires which are appropriately interconnected by standard braiding operations.

It is also known that, on account of its excellent mechanical properties, steel is the metal of choice for the said structure. However, its chemical properties are not excellent since it does not allow good  
25   adhesion to the vulcanized elastomeric material and it has poor corrosion resistance.

In order to overcome these drawbacks, steel is usually coated with a metal or a metal alloy layer.

Usually, said coating is a brass layer comprising about 70% by  
30   weight of copper and about 30% by weight of zinc. In this case the

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adhesion is promoted, thanks to the formation of a thin layer of copper sulphide  $\text{Cu}_x\text{S}$ , by the sulphur itself or by known derivatives thereof present in the vulcanization mixture as vulcanizing agents.

Even though, brass coated steel well adheres to a vulcanized elastomeric matrix, said adhesion decays in time because of the action of humidity and oxygen. Indeed in articles made of a vulcanized elastomeric material reinforced by brass coated steel wires optionally in the form of cords, such as, for example, tires, corrosion is caused both by humidity, which permeates the elastomer, and by water which comes into contact with the reinforcing structure made of brass coated steel through holes or tears in the elastomer.

Said brass/elastomer adhesion failure may be partially opposed by adding some cobalt in the form of a salt (US 5 356 711). It is believed that cobalt reduces the electrical conductivity of the layer of copper sulphide; this would slow the diffusion rate of  $\text{Zn}^{++}$  ions and, as a consequence, reduce the growing rate of the  $\text{ZnO}/\text{Zn}(\text{OH})_2$  interface layer which is responsible for the destruction of the  $\text{Cu}_x\text{S}$  film. As a result, some improvement in adhesion is obtained.

However, brass coated steel is slightly resistant to corrosion. This prompts to investigate different metal or alloy coatings.

US-4,651,513 describes a steel rope for reinforcing rubber products, such as tyres, this rope comprising a plurality of steel wires twisted together to form a multi-wire laminated rope having two or more successive layers of wire around a common core. The wires in the outermost layer are covered with a coating capable of adhering to rubber, for example brass, while the wires in the inner layer are covered with a corrosion-resistant coating, such as zinc on its own or as an alloy.

Among the various binary and ternary alloys mentioned in the said patent (col. 5, lines 49-54), mention is also made of a zinc/manganese

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alloy. However, the document does not exemplify or specify at any point what the manganese content of the said alloy is. In fact, the above patent indicates clearly that the most practical coating is one consisting solely of zinc (col. 5, lines 54-58).

5        EP-A-0 188 851 describes a steel reinforcing element for use in vulcanized rubber products, in which the said element is covered with a layer of coating capable of adhering to rubber, this layer being made of brass, with at least 50% copper and from 0.01 to 15% by weight of manganese.

10       In both of the above mentioned documents, the coating for the steel wire, whose function is to adhere to rubber, comprises brass (copper/zinc alloy with about 70% copper and about 30% zinc), alone or with manganese (ternary alloy).

15       However, the above mentioned coatings still suffer the drawbacks associated with copper.

Therefore, still there is a need to comply concurrently with both the requirements of a good resistance of the wire to corrosion and a good adhesion of the wire to a vulcanized elastomeric matrix.

20       It has now been found, surprisingly, that a coating made of a zinc/manganese binary alloy, in which the manganese content is of from 0.3 to 4.9% by weight, has, after age-hardening, improved corrosion resistance and greater adhesion to the vulcanized elastomeric material when compared with brass, with zinc on its own or with ternary alloys consisting of brass and manganese.

25       In a first aspect, the present invention thus relates to a surface-treated steel wire for reinforcing structures for articles of manufacture made of vulcanized elastomeric material, in which the said wire is coated with a layer of metal alloy and is characterized in that the said alloy is a zinc/manganese binary alloy comprising from 0.3 to 4.9% by  
30       weight of manganese.

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Preferably, the manganese content in the binary alloy of the present invention is of from 0.3 to 4.5% by weight, even more preferably from 1.5 to 4% by weight.

Typically, the said layer of surface coating is formed by  
5 electrodeposition on the surface of the said steel wire.

The thickness of the said layer of coating on the steel wire before drawing is preferably of from 1 to 4 microns. However, after drawing, the thickness of the said layer is typically of from 0.1 to 0.4 microns.

Preferred examples of zinc salts which are suitable for carrying out  
10 the electrodeposition process according to the invention are those chosen from the group comprising sulphate, sulphamate, hypophosphite, picrate, selenate and thiocyanate. Even more preferably, these are the sulphate and the sulphamate.

Preferred examples of manganese salts which are suitable for  
15 carrying out the electrodeposition process according to the invention are those chosen from the group comprising sulphates, sulphamates, acetates, formates, iodates, lactates, phosphates, selenates, thiocyanates, dithionates and valerates. Even more preferably, these salts are sulphates and sulphamates.

20 In a second aspect, the present invention relates to a process for the electrolytic deposition of a zinc/manganese binary alloy comprising from 0.3 to 4.9% by weight of manganese onto a steel wire passing through an electrolytic bath, characterized in that the said steel wire is passed through at least one electrolytic bath consisting of an aqueous solution  
25 of at least one salt chosen from zinc and manganese salts, the said electrolytic bath having:

- a temperature of from 20 to 50°C;
- a pH of from 2 to 6; and
- a cathode density of from 10 to 50 A/dm<sup>2</sup>.

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Typically, the throughput speed of the said wire is of from 10 to 70 m/min, even more typically of from 18 to 50 m/min.

Typically, the zinc salt and the manganese salt used in the process of the present invention are a sulphate.

5 Even more typically, the zinc sulphate is zinc sulphate heptahydrate and the manganese sulphate is manganese sulphate monohydrate.

In a preferred embodiment of the process of the present invention, the steel wire is immersed in a single electrolytic bath comprising a manganese salt and a zinc salt.

10 Preferably, the electrolytic bath of the preferred embodiment of the present invention has a temperature of from 25 to 40°C, a pH of from 3.0 to 4.5 and a cathode density of from 10 to 40 A/dm<sup>2</sup>.

In a second embodiment of the process of the present invention, the steel wire is immersed first in a first electrolytic bath comprising a  
15 manganese salt, then in a second electrolytic bath comprising a zinc salt, and lastly undergoes a thermal diffusion process.

Preferably, the first electrolytic bath also comprises a citrate. Even more preferably, the citrate is sodium citrate.

Preferably, the first electrolytic bath has a temperature of from 30 to  
20 40°C, a pH of from 4.5 to 5.5 and a cathode density of from 15 to 25 A/dm<sup>2</sup>.

Preferably, the second electrolytic bath has a temperature of from 20 to 30°C, a pH of from 2.5 to 3.5 and a cathode density of from 25 to 35 A/dm<sup>2</sup>.

25 Preferably, the thermal diffusion process is carried out by means of the Joule effect, by heating the wire for a period of from 5 to 10 seconds and at a temperature of from 450 to 500°C.

In both of the abovementioned embodiments, the electrolytic bath, consisting of an aqueous solution of at least one salt chosen from zinc

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and manganese salts, also comprises sodium citrate, sodium sulphate and magnesium sulphate heptahydrate.

In a third aspect, the present invention relates to a reinforcing structure for an article of manufacture made of a vulcanized elastomeric material, characterized in that it comprises at least one steel wire  
5 coated with a zinc/manganese binary alloy according to the present invention.

Further, in a fourth aspect, the present invention relates to a vulcanized elastomeric material, characterized in that it is reinforced by  
10 a structure comprising at least one steel wire coated with a zinc/manganese binary alloy according to the present invention.

Typically, said article is a tire, a conveyor belt, a transmission belt or a flexible hose.

Further, it has been surprisingly found that a steel wire surface-  
15 coated with a binary alloy of the present invention has a better adhesion to the vulcanized elastomeric matrix than a steel wire coated with brass when said vulcanized elastomeric matrix comprises a suitable adhesion promoter corresponding to at least 0.2% by weight of bivalent cobalt metal with respect to the weight of the elastomeric  
20 material.

Therefore, a further aspect this invention relates to an article of manufacture comprising at least one metal wire buried in a vulcanized elastomeric matrix obtained from a mixture comprising at least one vulcanizable elastomer and at least one vulcanizing agent consisting of  
25 sulphur or a derivative thereof, characterized in that said metal wire is made of steel coated with a zinc/manganese binary alloy comprising of from 0.3 to 4.9% by weight of manganese, and that said mixture further comprises a salt of bivalent cobalt in an amount corresponding to at least 0.2% by weight of bivalent cobalt metal with respect to the weight  
30 of said elastomer.



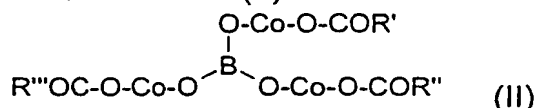
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Preferably, the amount of said salt of bivalent cobalt corresponds to an amount of bivalent cobalt metal of from 0.2 to 1% by weight with respect to the weight of said elastomer.

Preferably, said salt of bivalent cobalt is selected from the group  
5 comprising carboxylate compounds of formula (I)



wherein R is a C<sub>6-24</sub> aliphatic or aromatic group,  
cobalt-boron complexes of formula (II)



10 wherein R', R'' and R''', equal or different each other, are a C<sub>6-24</sub> aliphatic or aromatic group, and mixture thereof.

Preferred examples of R-CO-O-, R'-CO-O-, R''-CO-O- and R'''-CO-O- are those selected from the group comprising n-heptanoate, 2,2-dimethylpentanoate, 2-ethyl-pentanotate, 4,4-dimethyl-pentanoate, 2-ethyl-esanoate, n-octanoate, 2,2-dimethyl-esanoate, neodecanoate and naphthenate.

A preferred example of a salt of formula (I) is cobalt neodecanoate.

A preferred example of a salt of formula (II) is cobalt-boron 2-ethyl-esanoate-neodecanoate.  
20

Typically, the mixture may further comprise other conventional ingredients such as, for example, silica, resorcin and hexamethoxymethylamine.

The present invention is further illustrated by the following Examples  
25 and Figures which are intended to illustrate the present invention without limiting it in any way.

Figure 1 shows a wire cord of the present invention buried in a vulcanized elastomeric matrix;

Figure 2 is a sectional view of a tire in accordance with the invention;

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Figure 3 is a perspective view in section of a conveyor belt in accordance with the invention;

Figure 4 is a perspective view in section of a transmission belt in accordance with the invention;

5      Figure 5 is a perspective view in section of a flexible hose in accordance with the invention.

In particular, Figure 2 shows a tire made of a vulcanized elastomeric matrix and a reinforcing structure comprising at least one steel wire coated with a layer of a zinc/manganese binary alloy according to the present invention. In a preferred embodiment, the vulcanized  
10      elastomeric matrix of said tire is obtained from a mixture comprising at least one vulcanizable elastomer, at least one vulcanizing agent consisting of sulphur or a derivative thereof, and a salt of bivalent cobalt selected from the group comprising cobalt-boron 2-ethyl-esanoate-  
15      neodecanoate and cobalt neodecanoate according to the present invention.

Said tire is mounted on a rim 13, and is composed of: bead 10, bead core 12, carcass ply 14, belt 15, tread 16 and sidewalls 17. The belts  
20      15 are made of cords of steel wire coated with a layer of zinc/manganese binary alloy according to the present invention.

Figures 3 through 5 show a conveyor belt 20, a transmission belt 30 and a flexible hose 40, respectively, each of which is made of a vulcanized elastomeric matrix reinforced by cords 15 made of steel wires coated with a layer of zinc/manganese binary alloy according to  
25      the present invention. Preferably, in each of said articles the vulcanized elastomeric matrix is obtained from a mixture comprising at least one vulcanizable elastomer, at least one vulcanizing agent consisting of sulphur or a derivative thereof, and a salt of bivalent cobalt selected from the group comprising cobalt-boron 2-ethyl-esanoate-neode-  
30      canoate and cobalt neodecanoate according to the present invention.

In the following Examples the abbreviation 3x0.28 means a cord made of 3 wires 0.28 mm in diameter; the abbreviation 2+1x0.28 means a cord made of 2 wires 0.28 mm in diameter round which there is wound a third wire having the same diameter; the abbreviation  
 5 2+3x0.28 means a cord made of 2 strands, one made of 2 wires 0.28 mm in diameter and the second one made of 3 wires having the same diameter.

Other abbreviations used in the examples have the following meanings:

10 N.R. = natural rubber,  
 C.B. = carbon black,  
 HMMM = hexamethoxymethylmelamine  
 DCBS = N,N'-dicyclohexyl-2-benzothiazylsulphenamide.

The amounts of the components of the vulcanizable mixtures  
 15 exemplified are expressed in parts by weight.

#### EXAMPLE 1

##### One-stage deposition

A galvanic bath, capable of depositing on a steel wire a layer of a zinc/manganese binary alloy, according to the invention, consisting of  
 20 99.7% by weight of zinc and 0.3% by weight of manganese, has the following composition:

Zn <sup>++</sup>	1.13 mol/litre
Mn <sup>++</sup>	1.06 mol/litre
Mg <sup>++</sup>	0.25 mol/litre

25 The starting materials used to prepare the abovementioned bath were:

zinc sulphate heptahydrate	325 grams/litre
manganese sulphate monohydrate	180 grams/litre
magnesium sulphate heptahydrate	50 grams/litre

30 The operating conditions were:

- 10 -

bath temperature	30°C
pH of the bath	3.5
cathode current density (zinc anodes)	30 A/dm <sup>2</sup>
throughput speed of the wire	25 m/min

5 A layer of Zn/Mn binary alloy 1.8 microns thick was thus obtained.

## EXAMPLE 2

### One-stage deposition

A galvanic bath, capable of depositing on a steel wire a layer of a zinc/manganese binary alloy, according to the invention, consisting of  
 10 95.5% by weight of zinc and 4.5% by weight of manganese, has the following composition:

Zn <sup>++</sup>	1.13 mol/litre
Mn <sup>++</sup>	1.06 mol/litre
Na <sup>+</sup>	0.35 mol/litre

15 The starting materials used to prepare the abovementioned bath were:

zinc sulphate heptahydrate	325 grams/litre
manganese sulphate monohydrate	180 grams/litre
sodium citrate	30 grams/litre

20 The operating conditions were:

bath temperature	35°C
pH of the bath	4
cathode current density (zinc anodes)	15 A/dm <sup>2</sup>
throughput speed of the wire	15 m/min

25 A layer of Zn/Mn binary alloy 1.5 microns thick was thus obtained.

## EXAMPLE 3

### Two-stage deposition

A steel wire according to the invention was immersed first in a galvanic bath, capable of depositing 0.3% by weight of manganese,  
 30 having the following composition:

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Mn <sup>++</sup>	0.177 mol/litre
Na <sup>+</sup>	1.84 mol/litre

The starting materials used to prepare the abovementioned bath were:

5	manganese sulphate monohydrate	30 grams/litre
	sodium citrate	180 grams/litre

The operating conditions were:

	bath temperature	35°C
	pH of the bath	5
10	cathode current density (manganese anodes)	20 A/dm <sup>2</sup>
	throughput speed of the wire	70 m/min

A layer of Mn 0.005 microns thick was thus deposited.

The abovementioned steel wire was then immersed in a galvanic bath, capable of depositing 99.7% by weight of zinc, having the

15 following composition:

	Zn <sup>++</sup>	1.39 mol/litre
	Na <sup>+</sup>	0.70 mol/litre

The starting materials used to prepare the abovementioned bath were:

20	zinc sulphate heptahydrate	400 grams/litre
	sodium sulphate	50 grams/litre

The operating conditions were:

	bath temperature	25°C
	pH of the bath	3
25	cathode current density (zinc anodes)	30 A/dm <sup>2</sup>
	throughput speed of the wire	70 m/min

A layer of Zn 1.6 microns thick was thus deposited.

The steel wire was then subjected to thermal diffusion by means of the Joule effect, by heating it for 5-10 seconds at 500°C, thus obtaining

30 a layer of Zn/Mn binary alloy 1.6 microns thick.

## EXAMPLE 4

Two-stage deposition

A steel wire according to the invention was immersed first in a galvanic bath, capable of depositing 4.5% by weight of manganese, having the following composition:

Mn <sup>++</sup>	0.177 mol/litre
Na <sup>+</sup>	1.84 mol/litre

The starting materials used to prepare the abovementioned bath were:

manganese sulphate monohydrate	30 grams/litre
sodium citrate	180 grams/litre

The operating conditions were:

bath temperature	35°C
pH of the bath	5
cathode current density (manganese anodes)	20 A/dm <sup>2</sup>
throughput speed of the wire	60 m/min

A layer of Mn 0.07 microns thick was thus deposited.

The abovementioned steel wire was then immersed in a galvanic bath, capable of depositing 95.5% by weight of zinc, having the following composition:

Zn <sup>++</sup>	1.39 mol/litre
Na <sup>+</sup>	0.35 mol/litre

The starting materials used to prepare the abovementioned bath were:

zinc sulphate heptahydrate	400 grams/litre
sodium sulphate	50 grams/litre

The operating conditions were:

bath temperature	25°C
pH of the bath	3
cathode current density (zinc anodes)	30 A/dm <sup>2</sup>
throughput speed of the wire	60 m/min

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A layer of Zn 1.55 microns thick was thus deposited.

The steel wire obtained was subjected to thermal diffusion by means of the Joule effect, by heating it for 5-10 seconds at 500°C, thus obtaining a layer of Zn/Mn binary alloy 1.62 microns thick.

5

### EXAMPLE 5

#### Corrosion resistance

The corrosion resistance was determined by measuring the time required to initiate the formation of rust on five steel cords (each made of 3 wires 0.28 mm in diameter) coated according to the invention,  
10 immersed in aqueous 4% NaCl solution at 25°C.

The coatings had the following compositions:

- cord A: 99.7% zinc and 0.3% manganese;
- cord B: 99.3% zinc and 0.7% manganese;
- cord C: 99% zinc and 1% manganese;
- 15 cord D: 97.5% zinc and 2.5% manganese;
- cord E: 96% zinc and 4% manganese.

The results are given in Table 1.

Table 1

Coating	Time for formation of rust (minutes)
cord A	190
cord B	210
cord C	250
cord D	420
cord E	480

### COMPARATIVE EXAMPLE 1

20

#### Corrosion resistance

The process was performed as in Example 5 above, except that the test was carried out on four steel cords (each made of 3 wires 0.28 mm in diameter) coated according to the prior art.

The coatings had the following compositions:

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cord F: 70% copper, 29% zinc and 1% manganese  
(EP-A-0 188 851);

cord G: 70% copper, 26% zinc and 4% manganese  
(EP-A-0 188 851);

5 cord H: 67% Cu and 33% Zn (brass);

cord I: 100% zinc.

The results are given in Table 2.

Table 2

Coating	Time for formation of rust (minutes)
cord F	60
cord G	85
cord H	15
cord I	50

## EXAMPLE 6

10

Resistance to Corrosion

The corrosion resistance was also evaluated by measuring the ultimate tensile strength (T.S.) of the cords before and after aging simulated in two different conditions: in a climatic room at 65°C and 90% R.H. for 30 days (Test I) and in a so called "salty fog" room  
15 (aqueous 5% NaCl solution) at 40°C and 100% R.H. for 2 days (Test II). Steel wire cords coated with a layer (0.3 microns thick) of a Zn/Mn binary alloy (Mn content = 0.5%) of the present invention were compared with steel wire cords coated with a brass (67% Cu and 33% Zn) layer having the same thickness (0.3 microns) .

20 The results are given in Tables 3a and 3b.

Table 3a

2+1x0.28 Cord	T.S. decrease (%)	
	Zn/Mn	brass
Test I	30	41
Test II	19	41



Table 3b

	T.S. decrease (%)	
	Zn/Mn	brass
2+3x0.28 Cord		
Test I	9	25
Test II	4	15

## EXAMPLE 7

Adhesion to the vulcanized elastomeric material

The adhesion to the vulcanized elastomeric material was measured on test samples of vulcanized mixture on three types of steel cord of the invention (each made of 3 wires 0.28 mm in diameter), using the method described in "Kautschk und Gummi Kunststoffe", 5, 228-232, (1969), which measures the force required to remove a cord from a cylinder of vulcanized rubber.

The "pull-out force" was measured in Newtons using an electronic dynamometer. The values were measured both on freshly prepared vulcanized test samples and on test samples after age-hardening for one week at a temperature of 65°C and at 90% relative humidity (R.H.).

The composition of the mixture which formed the vulcanized rubber was, in parts % by weight, as follows:

natural rubber	100
ZnO	8
divalent cobalt	0.2
carbon black	50
silica	10
resorcinol	3
hexamethoxymethylenemelamine	2.4
dicyclohexylbenzothiazolesulphenamide	1.1
sulphur	4
trimercaptotriazine	0.5

The results are shown in Table 4.

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Table 4

ZnMn coating	Initial pull-out force (N)	$\pm$ SD (N)	End pull-out force (N)	$\pm$ SD (N)
Mn = 0.3%	321	26	254	18
Mn = 2%	330	18	260	19
Mn = 4%	327	26	247	21

SD = standard deviation

## COMPARATIVE EXAMPLE 2

Adhesion to the vulcanized elastomeric material

- 5 The process was performed in a similar manner to that of Example 7 above, except that test samples of mixture, having the abovementioned composition, vulcanized on two types of steel cord of the prior art (each made of 3 wires 0.28 mm in diameter) were used.

The results are shown in Table 5.

10

Table 5

Coating	Initial pull-out force (N)	$\pm$ SD (N)	End pull-out force (N)	$\pm$ SD (N)
Zn (100%)	300	24	195	20
brass*	332	27	261	22
CuZnMn**	318	19	248	20
CuZnMn***	303	22	231	21

SD = standard deviation.

\* Cu = 67% and Zn = 33%;

\*\* Cu = 70%, Zn = 29% and Mn = 1%;

\*\*\* Cu = 70%, Zn = 26% and Mn = 4%;

15

## EXAMPLE 8

Drawability

Three steel wires according to the invention (1.60 mm in diameter) were drawn to a final diameter of 0.28 mm at a speed of 16 m/sec in a

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device of the type HT 18 from the company Herborn. The number of metres of wire produced before the drawplate was consumed were measured. The weight percentage of loss of Zn/Mn alloy deposited was also measured.

5 Table 6 shows the results obtained.

Table 6

ZnMn coating	Metres of wire produced x 10 <sup>3</sup>	Loss of Zn/Mn alloy deposited (%)
Mn = 1%	2000	10
Mn = 2.5%	2000	10
Mn = 4.9%	2000	10

## COMPARATIVE EXAMPLE 3

Drawability

The process was performed in a similar manner to that of Example 8  
 10 above, except that three steel wires of the prior art were drawn.

Table 7 shows the results obtained.

Table 7

Coating	Metres of wire produced x 10 <sup>3</sup>	Loss of Zn/Mn alloy deposited (%)
ZnMn*	1000	20
brass**	2000	12
Zn (100%)	2000	10

\* Zn = 93% and Mn = 7%

\*\* Cu = 67% and Zn = 33%

15

## EXAMPLE 9

Vulcanized Elastomeric Material

Cylindrical test samples were prepared by burying steel wire cords (2+1x0.28, 2+3x0.28 and 3x0.28) coated with a zinc/manganese binary alloy layer (0.3 thick) of the present invention, in mixtures having the

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compositions shown herein below. The mixtures were then vulcanized at 151°C for 40 minutes.

The burial length of the cords in the test samples was 6 mm for 2+1x0.28 and 3x0.28 cords and 12 mm for 2+3x0.28 cords.

Ingredients	Mixture			
	A	B	C	D
N.R.	100	100	100	100
ZnO	5	5	5	5
C.B.	42	42	42	42
silica	13	13	13	13
aromatic oil	5	5	5	5
Co <sup>++</sup>	0.3 <sup>a)</sup>	0.5 <sup>a)</sup>	0.2 <sup>a)</sup>	0.2 <sup>b)</sup>
resorcin	2.5	2.5	2.5	2.5
HMMM	3.3	3.3	3.3	3.3
DCBS	0.8	0.8	0.8	0.8
sulphur	5	5	5	5
protective agents	3	3	3	3

- 5 a = as boron-cobalt 2-ethylhexanoate-neodecanoate;  
b = as cobalt neodecanoate.

#### EXAMPLE 10

##### Adhesion to Vulcanized Elastomeric Material

- 10 Adhesion was measured in a similar manner to that of Example 7 above, except that the test samples were prepared as described in the Example 9 above.

The pull out force was measured in Newtons with an electronic dynamometer.

- 15 The coating degree of the cords extracted from each test sample was graded according to a coating index ranking from 1 to 4 depending on the percent of the cord surface which was still well coated by elastomeric material.

- Initial adhesion values (Test I) and the adhesion values measured after having kept the test samples in a climatic room at 65°C and 90% R.H. for 8 days (Test II) are shown in the following Tables 8a, 8b and 8c where the first number is the adhesion value, as an average on 8 tests, while the index in brackets is the coating degree of the cords.

Table 8a

2+1x0.28 Cord <sup>(*)</sup>	Mixture		
	B	C	D
Test I	250 (4)	285 (4)	277 (4)
Test II	245(3.5)	258(3.5)	235(3.5)

(\*) made of wires coated with Zn/Mn binary alloy wherein Mn content was 0.5%.

Table 8b

2+3x0.28 Cord <sup>(*)</sup>	Mixture		
	B	C	D
Test I	658 (4)	659 (4)	669 (4)
Test II	454 (3)	436 (3)	350 (3)

- (\*) made of wires coated with Zn/Mn binary alloy wherein Mn content was 0.5%.

Table 8c

3x0.28 Cord <sup>(*)</sup>	Mixture	
	A	C
Test I	273 (4)	257 (4)
Test II	229(3.5)	190 (2)
3x0.28 Cord <sup>(**)</sup>	A	C
Test I	287 (4)	266 (4)
Test II	203(2.5)	188(2.5)

(\*) made of wires coated with Zn/Mn binary alloy wherein Mn content was 0.5%.

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(\*\*) made of wires coated with Zn/Mn binary alloy wherein Mn content was 1.1%.

## COMPARATIVE EXAMPLE 4

Adhesion to Vulcanized Elastomeric Material

- 5 The process was performed in a similar manner to that of the Example 10 above, except that there were used steel wires coated with brass (67% Cu and 33% Zn) buried in a vulcanized elastomeric matrix obtained by vulcanization of the mixtures described in the Example 9 above.
- 10 The results are shown in Table 9a, 9b and 9c.

Table 9a

2+1x0.28 Cord	Mixture		
	B	C	D
Test I	294 (4)	305 (4)	296 (4)
Test II	182 (3)	184 (3)	186 (3)

Table 9b

2+3x0.28 Cord	Mixture		
	B	C	D
Test I	731 (4)	736 (4)	739 (4)
Test II	263 (2)	287 (2)	265 (2)

Table 9c

3x0.28 Cord	Mixture	
	A	C
Test I	295 (4)	314 (4)
Test II	125 (2)	144 (2)

## CLAIMS

1. A surface-treated steel wire for reinforcing structures for articles of manufacture made of vulcanized elastomeric material, in which the said wire is coated with a layer of metal alloy, characterized in that  
5 the said alloy is a zinc/manganese binary alloy comprising from 0.3 to 4.9% by weight of manganese.
2. A surface-treated steel wire according to Claim 1, characterized in that the manganese content is of from 0.3 to 4.5% by weight.
3. A surface-treated steel wire according to Claim 2, characterized in  
10 that the manganese content is of from 1.5 to 4.0% by weight.
4. A surface-treated steel wire according to Claim 1, characterized in that the said layer of surface coating is formed by electrodeposition.
5. A reinforcing structure for an article of manufacture made of a vulcanized elastomeric material, characterized in that it comprises  
15 at least one steel wire coated with a zinc/manganese binary alloy according to any one of claims from 1 to 4.
6. An article of manufacture made of a vulcanized elastomeric material, characterized in that it is reinforced by a structure comprising at least one steel wire coated with a zinc/manganese bi-  
20 nary alloy according to any one of claims from 1 to 4.
7. An article of manufacture according to Claim 6, characterized in that it is a tire, a conveyor belt, a transmission belt or a flexible hose.
8. An article of manufacture comprising at least one metal wire buried in a vulcanized elastomeric matrix obtained from a mixture  
25 comprising at least one vulcanizable elastomer and at least one vulcanizing agent consisting of sulphur or a derivative thereof, characterized in that said metal wire is made of steel coated with a zinc/manganese binary according to any one of claims from 1 to 4, and that said mixture further comprises a salt of bivalent cobalt in

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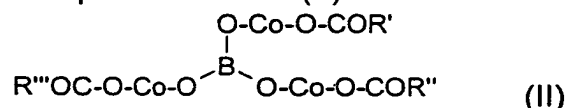
an amount corresponding to at least 0.2% by weight of bivalent cobalt metal with respect to the weight of said elastomer.

9. An article of manufacture according to Claim 8, characterized in that the amount of said salt of bivalent cobalt corresponds to an amount of bivalent cobalt metal of from 0.2 to 1% by weight with respect to the weight of said elastomer.

10. An article of manufacture according to claim 8 or 9, characterized in that said salt of bivalent cobalt is selected from the group comprising a carboxylate of formula (I)



wherein R is a C<sub>6-24</sub> aliphatic or aromatic group, a cobalt-boron complex of formula (II)



wherein R', R'' and R''', equal or different each other, are a C<sub>6-24</sub> aliphatic or aromatic group, and mixture thereof.

11. An article of manufacture according to claim 10, characterized in that R-CO-O-, R'-CO-O-, R''-CO-O- and R'''-CO-O- are selected from the group comprising n-heptanoate, 2,2-dimethylpentanoate, 2-ethyl-pentanoate, 4,4-dimethyl-pentanoate, 2-ethyl-esanoate, n-octanoate, 2,2-dimethyl-esanoate, neodecanoate and naphthenate.
12. An article of manufacture according to any of claims from 8 to 11, characterized in that the said salt of bivalent cobalt of formula (I) is cobalt neodecanoate.
13. An article of manufacture according to any of claims from 8 to 11, characterized in that the said salt of bivalent cobalt of formula (II) is cobalt-boron 2-ethyl-esanoate-neodecanoate.



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14. An article of manufacture according to any of claims from 8 to 13, characterized in that said article is a tire, a conveyor belt, a transmission belt or a flexible hose.
15. A process for the electrolytic deposition of a zinc/manganese binary alloy comprising from 0.3 to 4.9% by weight of manganese onto a steel wire passing through an electrolytic bath, characterized in that the said steel wire is passed through at least one electrolytic bath consisting of an aqueous solution of at least one salt chosen from zinc and manganese salts, the said electrolytic bath having:
  - a temperature of from 20 to 50°C;
  - a pH of from 2 to 6; and
  - a cathode density of from 10 to 50 A/dm<sup>2</sup>.
16. Process according to Claim 15, characterized in that the throughput speed of the said wire is of from 10 to 70 m/min.
17. Process according to Claim 15, characterized in that the zinc salt and the manganese salt are a sulphate.
18. Process according to Claim 17, characterized in that the zinc sulphate is zinc sulphate heptahydrate.
19. Process according to Claim 17, characterized in that the manganese sulphate is manganese sulphate monohydrate.
20. Process according to any one of Claims 15 to 20, characterized in that the steel wire is immersed in a single electrolytic bath comprising a manganese salt and a zinc salt.
21. Process according to any one of Claims 15 to 20, characterized in that the steel wire is immersed first in a first electrolytic bath comprising a manganese salt, then in a second electrolytic bath comprising a zinc salt, and lastly undergoes a thermal diffusion process.

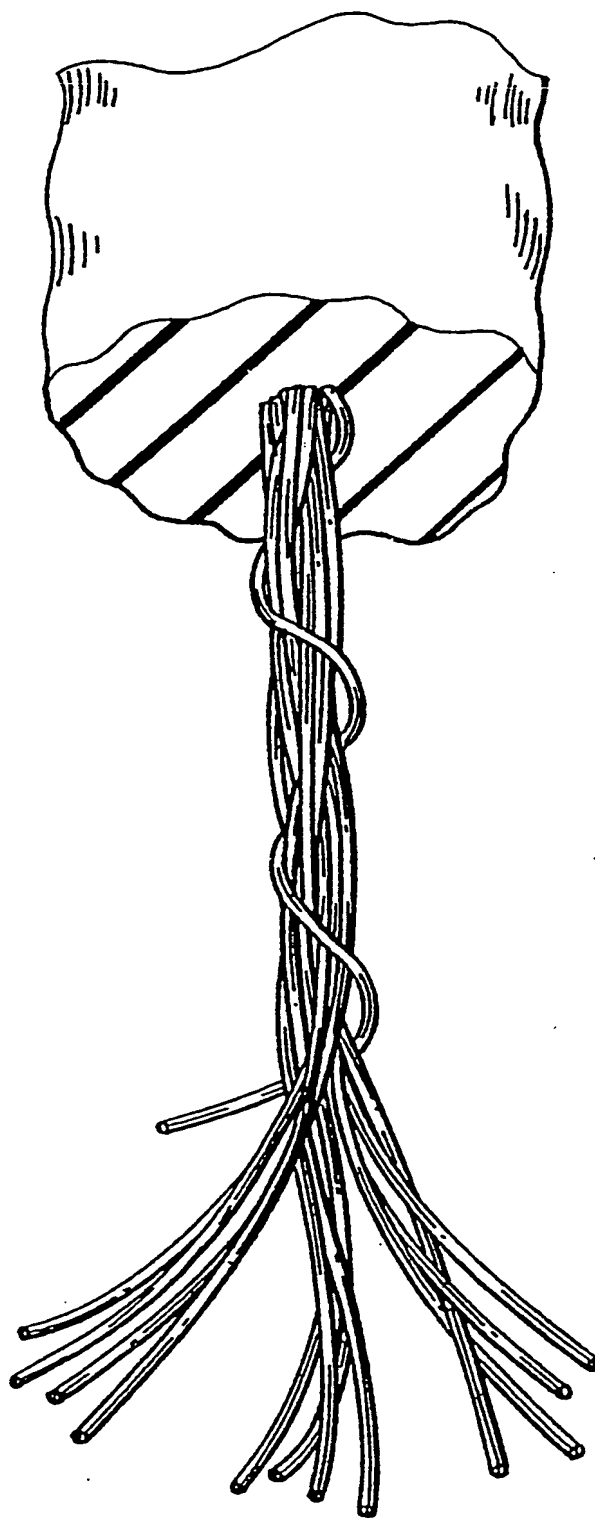


FIG. 1

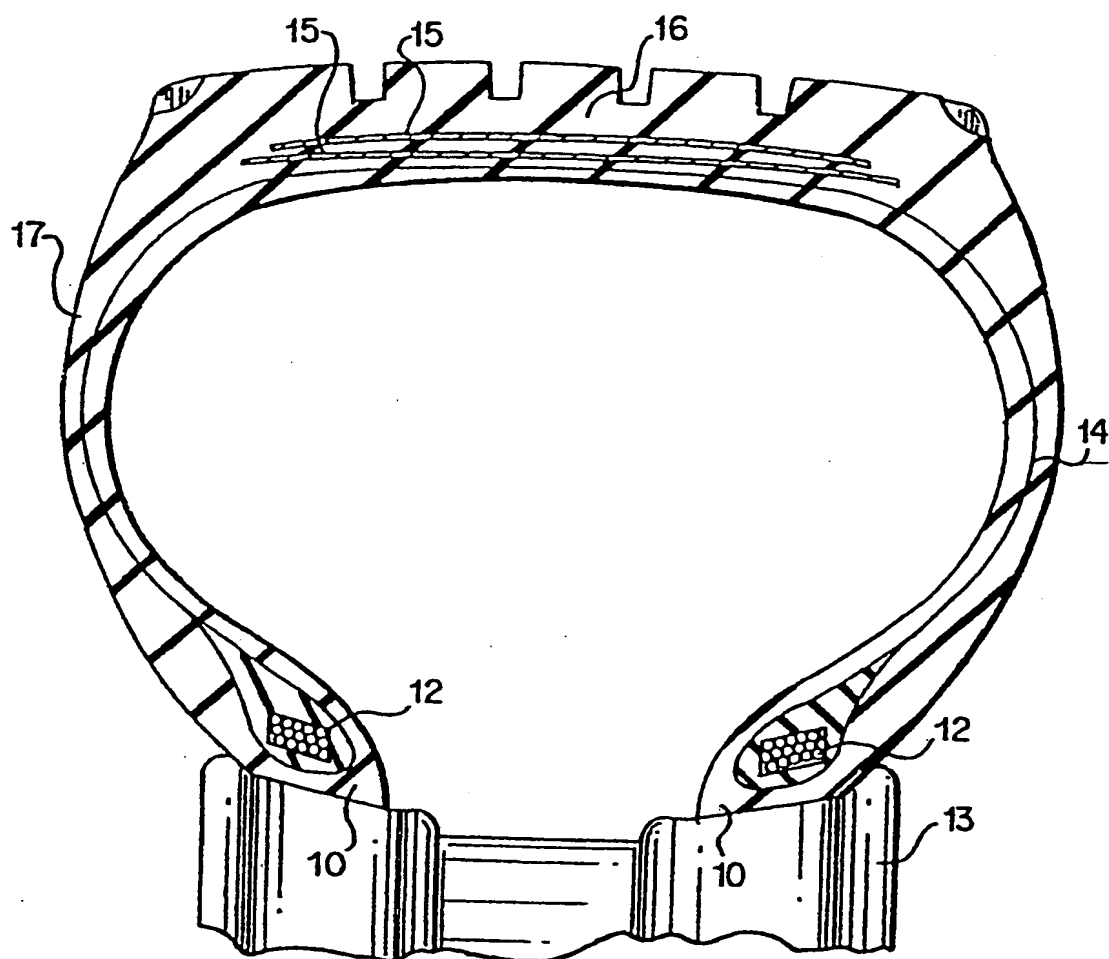


FIG. 2

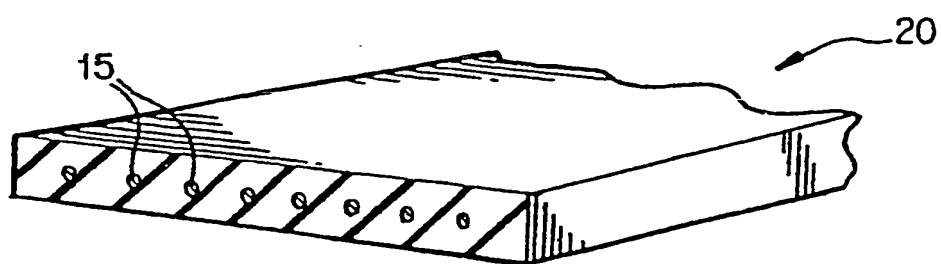


FIG. 3

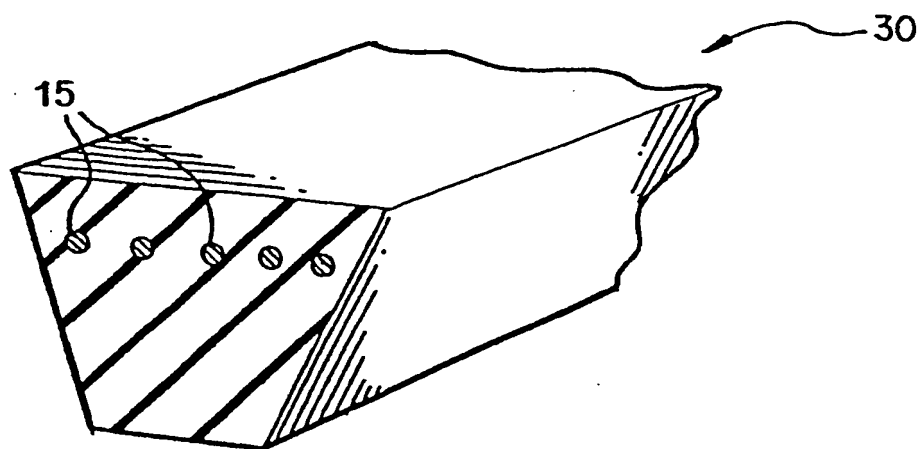


FIG. 4

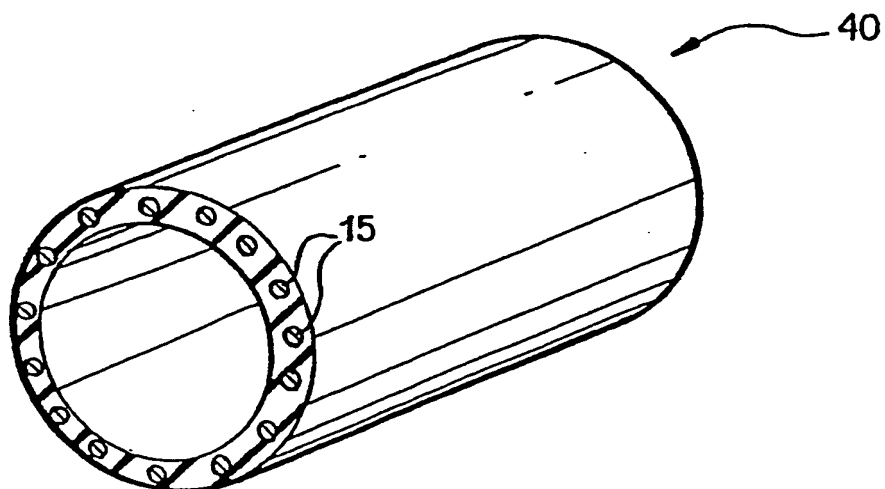


FIG. 5

# INTERNATIONAL SEARCH REPORT

Int. l. Application No

PCT/EP 99/00255

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C22C1/00 C25D3/56 C25D5/10 C25D5/50 B60C9/00  
B29B15/14

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C25D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 694 631 A (PIRELLI) 31 January 1996 see the whole document ---	1-21
A	EP 0 188 851 A (BEKAERT SA NV) 30 July 1986 cited in the application ---	
A	DATABASE WPI Section Ch, Week 8229 Derwent Publications Ltd., London, GB; Class M11, AN 82-60441E XP002074141 & JP 57 094590 A (WATANABE T) see abstract --- -/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

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Date of the actual completion of the international search

20 April 1999

Date of mailing of the international search report

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# INTERNATIONAL SEARCH REPORT

Int. Application No

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	<p>BOZZINI B ET AL: "ZN-MN ALLOY ELECTRODEPOSITION ON STEEL" TRANSACTIONS OF THE INSTITUTE OF METAL FINISHING, vol. 75, no. PART 05, September 1997, pages 175-180, XP000702194 -----</p>	
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Information on patent family members

International Application No

PCT/EP 99/00255

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